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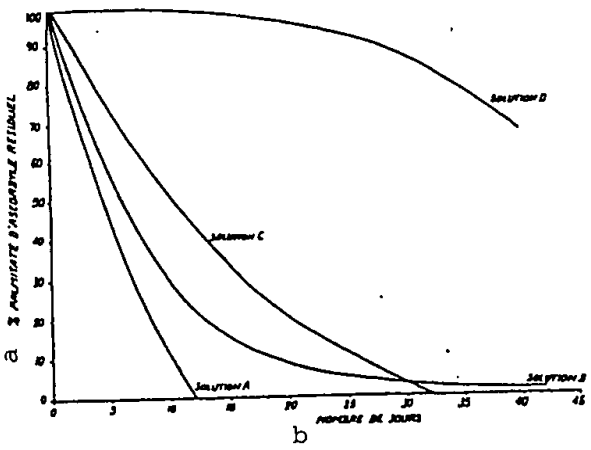
(54) New anti-oxidant system based on a stabilized ascorbyl ester, containing in combination at least one complexing agent and at least one thiol, and compositions containing this kind of anti-oxidant system.

(57) Anti-oxidant system based on at least one ascorbyl ester stabilized by at least one complexing agent and at least one thiol.

This system can contain in addition a tocopherol or caffeic acid or one of its esters.

Use in food compositions or in cosmetic compositions.



Key to Figure:
a = % Residual ascorbyl palmitate
b = vs. Number of days

EP 0 280 606 A1

Description

New anti-oxidant system based on a stabilized ascorbyl ester, containing in combination at least one complexing agent and at least one thiol, and compositions containing this kind of anti-oxidant system.

The present invention has as its subject a new anti-oxidant system based on a stabilized ascorbyl ester containing, in combination, at least one complexing agent and at least one thiol, the use of this kind of anti-oxidant system and of compositions based on oleaginous substances containing this kind of anti-oxidant system, in particular cosmetic compositions.

It is known that fatty substances have a tendency to become oxidized, even at ambient temperature, and this oxidation (or rancidity) causes them to take on new properties, in particular of taste and smell, which are generally considered to be undesirable when these fatty substances are for example incorporated into food compositions or into cosmetic compositions.

Thus, protective agents that in fact act as anti-oxidants are currently used in compositions containing fatty substances.

Among the known anti-oxidants, ascorbic acid which acts in particular by the direct absorption of oxygen, is currently used. However, ascorbic acid is fairly insoluble in fats and is thus difficult to use to protect them from oxidation.

In order to solubilize the ascorbic acid molecule in fatty substances, it has been proposed to use various ascorbyl esters such as lauryl stearate, palmitate or laurate; see for example the article by C.F. BOURGEOIS, Revue Francaise des Corps Gras, No. 9, pages 353-356 (September 1981).

It is known that besides their specific anti-oxidant properties, ascorbic acid derivatives also have the property of improving the activity of anti-oxidant agents such as the tocopherols or caffeic acid and its esters, by favoring the regeneration of these anti-oxidant agents; see for example H.S.OLCOTT, Oil Soap 18, (1941) 77 and US patent 2,462,663.

Various improvements in these binary anti-oxidant agents have also been proposed, of the type of ascorbic derivative + tocopherols or ascorbic acid derivatives + caffeic acid derivatives, providing for the addition of a third constituent further improving the anti-oxidant effects. Among the third constituents of these ternary systems may be cited in particular p-aminobenzoic acid (US patent 2,462,663), phospholipids (R.W. RIEMENSCHNEIDER et al., Oil Soap 47 (1944)), amines (KLAUI, The Functional (Technical) Uses of Vitamins, M. Stein, Ed., University of Nottingham Seminar Vitamins, London, England (1971), page 110), etc.

It has now been discovered that it is possible to improve the anti-oxidant properties of ascorbyl esters considerably by using these anti-oxidants in conjunction with at least one complexing agent and/or at least one thiol. A significant effect of synergy is then observed.

The present invention thus has as its subject a new anti-oxidant system based on at least one stabilized ascorbyl ester, characterized by the fact that it includes at least one complexing agent and at least one thiol.

The ascorbyl ester is of course a fat-soluble ester, and in particular an ester of an aliphatic acid having 6 to 24 carbon atoms such as ascorbyl stearate, palmitate, or laurate.

The term complexing agent is understood to mean a compound that is capable of inhibiting by chelation the catalytic effect of transition metals in the free state in the medium.

Among the complexing agents that can be used may be cited in particular ethylenediamine tetraacetic acid (EDTA), the pentasodium salt of diethylenetriamine pentaacetic acid, hexadecylamine salicylate (HDAS), citric acid, tartaric acid and its sodium salt, phytic acid, dibenzoyldithiocarbamate or their mixtures.

In addition to at least one of these complexing agents, the invention composition may also contain a secondary complexing agent such as sorbitol.

According to the present patent application, a thiol is understood to be a reducing compound that contributes to keeping the ascorbyl esters in their reduced form.

Among the thiols that can be used according to the invention may be cited in particular N-acetyl-cysteine, glutathione or their mixtures.

The new anti-oxidant system as defined above can be presented in the form of an oily liquid composition; or the anti-oxidant system can be presented in the form of an alcoholic solution such as an ethanolic solution.

In the invention anti-oxidant system, the relative proportions of the three categories of principal constituents depend in particular on the molecular masses of the complexing agent and of the thiol. Generally, the thiol is present in a proportion of 1 to 37.5% and the complexing agent in a proportion of 2 to 25% by weight relative to the total weight of these three types of constituents.

When a secondary complexing agent is used at the same time as the main complexing agent, it is present in a proportion such that the mixture is between 2 and 25% by weight.

The ascorbyl ester is generally present in the three-constituent anti-oxidant system in a proportion of between 5 and 87.5% by weight.

The invention also has as its subject an anti-oxidant system as defined above which contains in addition another anti-oxidant chosen from among the tocopherols and caffeic acid (or 3,4-dihydroxycinnamic acid), or its esters.

"Tocopherols" is understood to mean not only α-tocopherol, but also β, γ, or δ-tocopherols well as their mixtures.

Among the esters of caffeic acid may be cited the alkyl esters such as the methyl, ethyl, or butyl esters and the phytol ester.

It has been observed in a quite surprising manner that in such combinations the anti-oxidant activity of the tocopherols and of caffeic acid results from a significant synergic effect thanks to the presence of the ascorbyl ester stabilized by the complexing agent-thiol pair.

According to this form of execution of the invention, the anti-oxidant system is preferably constituted of:

0.5 to 20% tocopherol(s) or
caffeic acid (or one of its esters)
8 to 70% ascorbyl ester
4 to 20% complexing agent
2 to 30% thiol.

The molar ratio of ascorbyl ster to the tocopherol(s) or caffeic acid or one of its esters should preferably be higher than or equal to 3.

This synergic effect can also be improved, when the anti-oxidant system is based on tocopherol(s), by combining a polypeptide with it.

According to this second form of execution, the content of polypeptide is preferably between 1.5 and 80%.

The weight ratio of polypeptide to tocopherol(s) should preferably be higher than or equal to 3.

The polypeptides have an average molecular weight between about 1000 and about 100,000. Among these the following may be mentioned in particular:

(a) The polypeptide sold under the name "KERASOL" (soluble keratin polypeptide of average molecular weight about 100,000) by CRODA Chemicals Ltd.

b) The polypeptide sold under the name "Polypeptide SF" (a polypeptide of partially neutralized animal collagen of average molecular weight about 1000) by the NAARDEN company.

(c) The polypeptide sold under the name "Polypeptide LSN" (a polypeptide of animal collagen in the form of the ammonium salt containing about 3% (max) of inorganic salt) by the NAARDEN company,

(d) The polypeptide sold under the name "LACTOLAN" (a polypeptide obtained starting from fresh, previously defatted cow's milk,) by LABORATOIRES SEROBIOLOGIQUES of NANCY.

The invention also has as its subject compositions containing fatty substances, characterized by the fact that they contain at least one anti-oxidant system as defined previously.

The invention compositions can be in particular food compositions (edible oils, lard, butter, margarine or other butter substitutes) or cosmetic compositions.

The fatty substances present in the cosmetic compositions of the invention are for example fats of animal origin such as cetine (spermaceti), beeswax, lanolin, perhydrosqualene, turtle oil, etc.; vegetable fats in the forms of oils, fats or waxes such as sweet almond oil, avocado oil, olive oil, etc.; hydrogenated coconut or palm kernel oil, cocoa butter, carnauba wax, montana wax; as well as the synthetic oils constituted by esters and/or ethers of glycerol or glycol such as those described in the French patents Nos. 75.24656, 75.24657, and 75.24658.

In addition to more or less oxidizable fatty substances, the cosmetic compositions can contain products sensitive to oxidation such as vitamin F or β-carotene.

The cosmetic compositions according to the invention are presented in the form of oily solutions, emulsions, solid products or lotions. They constitute in particular milks for skin care, creams (creams for the face, hands, body, suntan creams, cleansing creams, foundation creams), liquid foundations, cleansing milks, suntan milks, bath oils, lipsticks, eyeshadows, deodorant sticks, etc.

According to a preferred form of execution, the cosmetic compositions are presented in the form of creams intended for the protection of the skin lipids from oxidation.

In the cosmetic compositions according to the invention, the anti-oxidant system as defined above is generally present so as to have the following proportions relative to the total weight of the composition:

Tocopherol(s)
or
Caffeic acid (or one of its esters) 0 to 0.5%
preferably 0.05 to 0.5%
Ascorbyl ester 0.45 to 1.6%
Complexing agent 0.2 to 0.5%
Thiol 0.1 to 0.7%

When the anti-oxidant system is based on tocopherol(s), the proportion of polypeptide possibly present is then between 0.05 and 8% relative to the total weight of the composition.

The invention compositions can contain in addition active compounds or ingredients commonly used in the compositions mentioned above, such as surfactant agents, coloring agents, perfumes, astringent products, ultra-violet-absorbing products, organic solvents, water, etc.

These compositions are prepared by the usual methods.

Several examples of anti-oxidant systems in accordance with the invention will now be given as an illustration, as well as examples of cosmetic compositions containing these anti-oxidant systems.

Example 1
Ascorbyl palmitate 76%
Citric acid 16%
N-Acetylcysteine 8%

Example 2
Ascorbyl palmitate 73%
Citric acid 9%
Glutathione 9%
N-Acetylcysteine 9%

Example 3
Ascorbyl palmitate 79%
Citric acid 5%
EDTA 12%
N-Acetylcysteine 4%

Example 4
Tocopherols (mixture of α, β, γ, and δ) 7%
Ascorbyl palmitate 65%
Citric acid 7%
EDTA 13%
N-Acetylcysteine 9%

Example 5
Tocopherols 11%
Ascorbyl palmitate 65%
Hexadecylamine salicylate 6%
Sorbitol 9%
N-Acetylcysteine 9%

Example 6
Tocopherols 16%
Ascorbyl palmitate 63%
Glutathione 6%
N-Acetylcysteine 3%
Citric acid 3%
EDTA 9%

Example 7
Caffeic acid 8%
Ascorbyl palmitate 49%
Citric acid 4%
EDTA 10%
Glutathione 10%
N-Acetylcysteine 19%

Example 8
Caffeic acid 7%
Ascorbyl palmitate 65%
Sodium tartrate 8%
N-Acetyl-cysteine 20%

Example 9
Caffeic acid 8%
Ascorbyl palmitate 70%
Hexadecylamine salicylate 15%
N-Acetylcysteine 7%

Example 10
Tocopherols 9%
Ascorbyl palmitate 36%
Citric acid 4.5%
N-Acetylcysteine 4.5%
EDTA 1.5%
"KERASOL" polypeptide (active substance) 44.5%

Example 11
Tocopherols 5%
Ascorbyl palmitate 21.5%
Citric acid 2.5%
N-Acetylcysteine 1%
Glutathione 1%
EDTA 2.5%
"Polypeptide SF" polypeptide (active substance) 66.5%

EXAMPLES OF COSMETIC COMPOSITIONS

I - Water-in-oil emulsion skin cream

- Magnesium lanolate ..... 14.4 %
- Lanolin alcohol ..... 3.6 %
- Sunflower oil ..... 40.0 %
- Isopropyl myristate ..... 8.0 %
- Ozokerite ..... 4.0 %
- Vitamin F ..... 2.0 %
- Ascorbic acid ..... 0.5 %
- Soybean lecithin ..... 5 %

- Tocopherols ..... 0.25 %
- Ascorbyl palmitate ..... 1.0 %
- Glutathione ..... 0.1 %
- N-Acetylcysteine ..... 0.05 %
- Citric acid ..... 0.05 %
- EDTA ..... 0.15 %

- Perfume ..... 0.8 %
- Methyl parahydroxybenzoate ..... 0.3 %
- Water ..... qsp 100 % by weight

II - Anhydrous balm

- Shea oil ..... 60.0 %
- Sunflower oil ..... 20.0 %
- Vitamin F ..... 2.0 %
- Soybean lecithin ..... 4.9 %
- Tocopherols ..... 0.2 %
- Ascorbyl palmitate ..... 1.13 %
- Glutathione ..... 0.35 %
- Citric acid ..... 0.15 %
- N-Acetylcysteine ..... 0.35 %
- EDTA ..... 0.15 %

- Vaseline ..... qsp 100 % by weight

III - Oil for the face and body

- Shea oil ..... 2.0 %
- Sunflower oil ..... 31.8 %
- Vitamin F ..... 2.0 %
- Soybean oil ..... 32.0 %

- Tocopherols ..... 0.1 %
- Citric acid ..... 0.05 %
- Ascorbyl palmitate ..... 1.0 %
- N-Acetylcysteine ..... 0.1 %
- EDTA ..... 0.15 %

- Soybean lecithin ..... 0.1 %
- Peanut oil ..... qsp 100 % by weight

IV - Oil-in-water emulsion skin cream

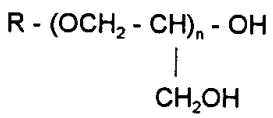
- Sorbitan monostearate with 20 moles ethylene oxide (Tween 60) ..... 1.0 %
- Glycerol stearate ..... 2.0 %
- Stearic acid ..... 1.4 %
- Triethanolamine ..... 0.7 %
- Cetyl alcohol ..... 0.5 %
- Sunflower oil ..... 15.0 %
- Vitamin F ..... 2.0 %
- Ascorbic acid ..... 1.0 %
- Soybean lecithin ..... 0.6 %
- Paraffin oil 2.4%

- Caffeic acid 0.2%
- Ascorbyl palmitate ..... 1.5 %
- Hexadecylamine salicylate ..... 0.5 %
- N-Acetylcysteine ..... 0.3 %

- Carboxyvinyl polymer sold under the name "Carbopol 940" by the Goodrich Co. ..... 0.2 %
- Triethanolamine 0.2%
- Perfume ..... 0.8 %
- Preservative (methyl parahydroxybenzoate) .... 0.25 %
- Water ..... qsp 100 % by weight

V. Body care fluid

- Non-ionic amphiphilic lipid of general formula



in which R is a hexadecyl radical and n has an average statistical value equal to 3 ..... 4.5%
- Cholesterol ..... 4.5 %
- Dicetylphosphate ..... 1.0 %
- Methyl parahydroxybenzoate ..... 0.3 %
- Sterile demineralized water ..... 30.0 %

2nd PHASE

To the dispersion of spherules obtained in the first phase are added the following substances:
- Perfume 0.4%
- Sunflower oil ..... 10.0 %
- Paraffin oil ..... 4.0 %
- Vitamin F ..... 2.0 %
- Soybean lecithin ..... 1.0 %

- Caffeic acid ..... 0.1 %
- Ascorbyl palmitate ..... 1.0 %
- Hexadecylamine salicylate ..... 0.2 %
- N-Acetylcysteine ..... 0.1 %

- Carboxyvinyl polymer sold Under the name "Carbopol 940 by the Goodrich Co. ..... 0.4 %
- Triethanolamine ..... 0.4 %
- Demineralized water ..... qsp 100 % by weight

VI - Suntan cream

- Magnesium lanolate ..... 7.2 %
- Lanolin alcohol ..... 1.8 %
- Sunflower oil ..... 20.6 %
- Vitamin F ..... 2.0 %
- β-Carotene ..... 0.1 %
- Soybean lecithin ..... 0.4 %
- Paraffin oil ..... 4.0 %

- Caffeic acid ..... 0.1 %
- Ascorbyl palmitate ..... 0.4 %
- Citric acid ..... 0.05 %
- Glutathione ..... 0.05 %
- N-Acetylcysteine ..... 0.05 %
- EDTA ..... 0.15 %

- Ascorbic acid ..... 1 %
- Polyethylene powder ..... 10.0 %
- 2-Phenyl-benzimidazole 5-sulfonic acid sold under the name "EUSOLEX 232" by the Merck Co. ..... 3.0 %
- 2-Hydroxy-4-methoxy-benzophenone sold under the Name "UVINUL M40" by BASF ..... 3.0 %
- Perfume ..... 1.0 %
- Methyl parahydroxybenzoate ..... 0.15 %
- Propyl parahydroxybenzoate ..... 0.15 %
- Water ..... qsp 100 % by weight

VII - Oil for the face and body

- Shea oil ..... 2.0 %
- Sunflower oil ..... 31.8 %
- Vitamin F ..... 2.0 %
- Soybean oil ..... 32.0 %

- Tocopherols ..... 0.3 %
- Citric acid ..... 0.15 %
- Ascorbyl palmitate ..... 1.2 %
- N-Acetylcysteine ..... 0.15 %
- EDTA ..... 0.05 %
- "KERASOL" polypeptide (active substance) ..... 1.5 %
- Soybean lecithin ..... 0.1 %
- Peanut oil ..... qsp 100 % by weight

VIII - "Water-in-oil emulsion" skin cream

- Magnesium lanolate ..... 14.4 %
- Lanolin alcohol ..... 3.6 %
- Sunflower oil ..... 40.0 %
- Isopropyl myristate ..... 8.0 %
- Ozokerite ..... 4.0 %
- Vitamin F ..... 2.0 %
- Ascorbic acid ..... 0.6 %
- Soybean lecithin ..... 5 %

- Tocopherols ..... 0.2 %
- Ascorbyl palmitate ..... 0.9 %
- Glutathione ..... 0.05 %
- N-Acetylcysteine ..... 0.05 %
- Citric acid ..... 0.1 %
- EDTA ..... 0.1 %
- "Polypeptide SF" polypeptide (active substance) . 2.8 %

- Perfume ..... 0.8 %
- Methyl parahydroxybenzoate ..... 0.3 %
- Water ..... qsp 100 % by weight

1 - Study of the stabilization of the ascorbyl palmitate

In order to determine the stabilizing effect of the complexing agent-thiol pair on ascorbyl palmitate, several solutions in ethanol were studied.

The determination, over time, of the rate of degradation of the ascorbyl palmitate was effectuated by HPLC. The solutions studied were the following:

Solution A:
0.05% Ascorbyl palmitate

Solution B:
0.05% Ascorbyl palmitate
0.01% N-Acetylcysteine

Solution C:
0.05% Ascorbyl palmitate
0.01% EDTA

Solution D:
0.05% Ascorbyl palmitate
0.01% N-Acetylcysteine
0.01% EDTA

The results obtained are reported in Figure 1.

As can be observed, as a function of the curve corresponding to Solution D, the rate of degradation of the ascorbyl palmitate is very clearly lower than the other solutions, which demonstrates the stabilizing character of the complexing agent (EDTA)-thiol (N-acetylcysteine) pair.

In fact, after 40 days, the rate of degradation of the ascorbyl palmitate in Solution D is only about 30% whereas for solutions A, B and C, the ascorbyl palmitate is completely degraded after the same period.

2 - Study of the effect of the synergy between ascorbyl palmitate, stabilized with the mixture HDAS + acetyl-cysteine, and the tocopherols.

The oil used in this test is Vitamin F.

Mixtures were prepared of Vitamin F with various quantities of tocopherols, ascorbyl palmitate, hexadecylamine salicylate (HDAS) and N-acetylcysteine. The quantities are given in detail in Table I below; they are expressed in % and are relative to the same quantity (100 g) of Vitamin F.

The samples studied are brought to 100°C with air bubbled in (20 l/hr) so as to effectuate an accelerated oxygenation of the oil.

The concentration of volatile acids resulting from the degradation of the hydroperoxides and aldehydes formed by oxidation is then followed continuously in a water-filled cell in which a platinum electrode is immersed. This electrode measures the course of the conductivity as a function of time. Oxidation causes an increase in the conductivity.

The induction time, which represents the period at the end of which the oxidation starts, is determined by the intersection of the two tangents to the autooxidation curve.

TABLE I

Ascorbyl palmitate	HDAS*	N-Acetylcysteine	Tocopherols	Induction Time
-	-	-	0.20	60 min.
0.20	-	-	-	20 min.
0.20	-	-	0.20	92 min.
-	0.20	0.10	-	15 min.
0.20	0.20	-	0.20	93 min.
0.20	-	0.10	0.20	96 min.
0.20	0.20	0.10	0.20	114 min.

* hexadecylamine salicylate

The induction time of the Vitamin F alone, without an anti-oxidant agent, is 15 mins.

Table I shows that the combination of hexadecylamine salicylate and N-acetylcysteine, alone, does not produce any effect. On the other hand, as is known, the combination alpha-tocopherol + ascorbyl palmitate brings a significant improvement in the induction time. This induction time is again significantly improved by the hexadecylamine salicylate + N-acetylcysteine combination, while each of these agents added alone to the mixture of alpha-tocopherol and ascorbyl palmitate is practically without influence.

3 - Study of the effect of the synergy between ascorbyl palmitate, stabilized by the mixture HDAS + N-acetylcysteine, and caffeic acid

The trial is carried out as before. The results are collected in Table II.

TABLE II

Ascorbyl palmitate	HDAS	N-acetylcysteine	Caffeic acid	Induction Time
0.25	-	-	0.10	93 min
0.21	0.21	0.10	0.10	315 min.

Table II shows the synergic effect brought by the addition to the system studied of the combination hexadecylamine salicylate + N-acetylcysteine.

This combination considerably increases the induction time of the system caffeic acid + ascorbyl palmitate, whereas when used alone this combination, as was shown in the Table I above, has no effect.

Claims

1. Anti-oxidant system based on at least one stabilized ascorbyl ester, characterized by the fact that it contains at least one complexing agent and at least one thiol.

2. Anti-oxidant system in accordance with claim 1, characterized by the fact that the ascorbyl ester is an ester of an aliphatic acid having from 6 to 24 carbon atoms such as ascorbyl stearate, palmitate or laurate.

3. Anti-oxidant system in accordance with claim 1, characterized by the fact that the complexing agent is ethylenediamine tetraacetic acid, the pentasodium salt of diethylenetriamine pentaacetic acid, hexadecylamine salicylate, citric acid, tartaric acid, sodium tartrate, phytic acid, dibenzyldithiocarbamate or their mixtures.

4. Anti-oxidant system in accordance with any one of the preceding claims, characterized by the fact that it contains in addition a secondary complexing agent such as sorbitol.

5. Anti-oxidant system in accordance with claim 1, characterized by the fact that the thiol is N-acetylcysteine, glutathione or their mixtures.

6. Anti-oxidant system in accordance with claim 1 or 2, characterized by the fact that the ascorbyl ester is present in an amount of 5 to 87.5% by weight.

7. Anti-oxidant system in accordance with any one of the preceding claims, characterized by the fact that the complexing agent is present in a proportion of 2 to 25% by weight and that the thiol is present in a proportion of 1 to 37.5% by weight.

8. Anti-oxidant system in accordance with any one of the preceding claims, characterized by the fact that it contains in addition at least one tocopherol or a mixture of tocopherols.

9. Anti-oxidant system in accordance with claim 8, characterized by the fact that it contains in addition a polypeptide, the weight ratio of polypeptide to the tocopherol(s) being higher than or equal to 3.

10. Anti-oxidant system in accordance with any one of the claims 1 to 7, characterized by the fact that it contains in addition caffeic acid or one of its esters.

11. Anti-oxidant system in accordance with any one of the preceding claims, characterized by the fact that it is constituted of:

    0.5 to 20% tocopherol(s) or caffeic acid
    (or one of its esters)
    8 to 70% ascorbyl ester
    4 to 20% complexing agent
    2 to 30% thiol.

12. Anti-oxidant system in accordance with any one of the claims 1 to 9 and 11, characterized by the fact that it is constituted of:

    0.5 to 20% tocopherol(s)
    8 to 70% ascorbyl ester
    4 to 20% complexing agent
    2 to 30% thiol
    1.5 to 80% polypeptide.

13. Anti-oxidant system in accordance with any one of the preceding claims, characterized by the fact that molar ratio of the ascorbyl ester to the tocopherol(s) or to the caffeic acid or one of its esters is higher than or equal to 3.

14. Composition containing fatty substances, characterized by the fact that it contains an anti-oxidant system in accordance with any one of the claims 1 to 13.

15. Cosmetic composition characterized by the fact that it contains an anti-oxidant system in accordance with any one of the claims 1 to 13, the proportions of the constituents of the anti-oxidant system relative to the total weight of the composition being:

Tocopherol(s)
or
Caffeic acid (or one of its esters) 0 to 0.5%
preferably 0.05 to 0.5%
Ascorbyl ester 0.45 to 1.6 %
Complexing agent 0.2 to 0.5%
Thiol 0.1 to 0.7%.

16. Cosmetic composition in accordance with claim 15, characterized by the fact that the proportions of the constituents of the anti-oxidant system relative to the total weight of the composition are:

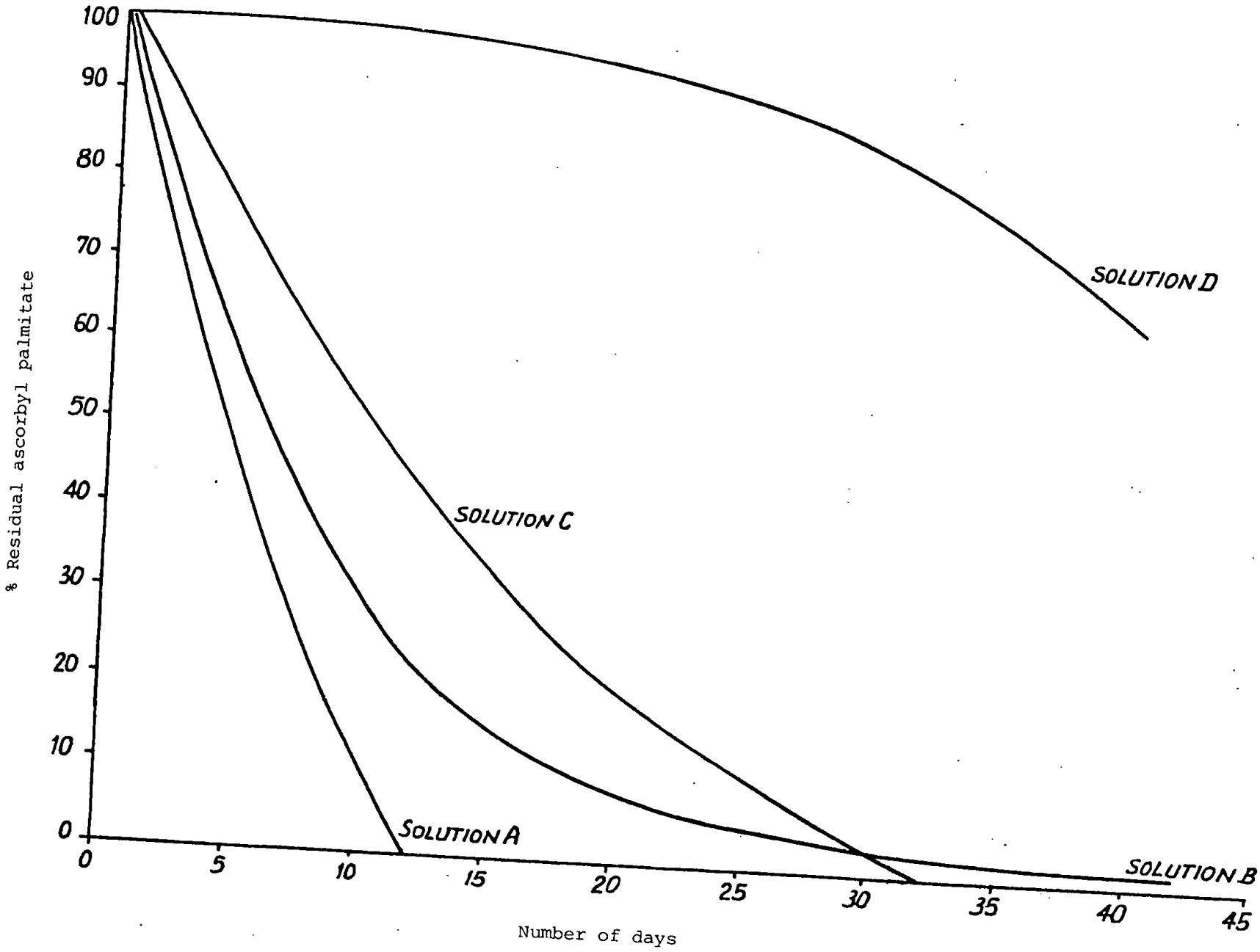
Tocopherol(s) 0.05 to 0.5%
Ascorbyl ester 0.45 to 1.6 %
Complexing agent 0.2 to 0.5%
Thiol 0.1 to 0.7%
Polypeptide 0.05 to 8%.

17. Cosmetic composition in accordance with any one of the claims 15 and 16, characterized by the fact that the ascorbyl ester is ascorbyl palmitate.

18. Cosmetic composition in accordance with any one of the claims 15 to 17, characterized by the fact that the complexing agent is ethylenediamine tetraacetic acid, hexadecylamine salicylate, citric acid, the pentasodium salt of diethylenetriamine pentaacetic acid, tartaric acid or its sodium salt, phytic acid, or dibenzylthiocarbamate or a mixture of these substances.

19. Cosmetic composition in accordance with any one of the claims 15 to 17, characterized by the fact that the thiol is N-acetylcysteine, glutathione or their mixtures.

20. Cosmetic composition in accordance with any one of the claims 15 to 19, characterized by the fact that it is presented in the form of a cream intended for the protection of the lipids of the skin from oxidation.


% Residual ascorbyl palmitate
100
90
80
70
60
50
40
30
20
10
0
0
5
10
15
20
25
30
35
40
45
Number of days
SOLUTION D
SOLUTION C
SOLUTION A
SOLUTION B

EUROPEAN PATENT OFFICE

EUROPEAN SEARCH REPORT

Application No. EP 88 40 0283

DOCUMENTS CONSIDERED PERTINENT			
Category	Reference of document with indication of pertinent parts if necessary	Claim involved	CLASSIFICATION OF THE PATENT (Int. Cl. 4)
A	FR-A-1 438 158 (LEROI) * Summary; Column 1, Line 20-23 *	1	C 09 K 15/12 A 61 K 7/48 A 61 K 7/06
A	DE-B-1 239 063 (H. JANISTYN) * Claim *	1	
A	FR-A-2 282 266 (PHARMACIA AB) * Claim *	1	
A	DE-A-2 550 648 (SHEFFNER) * Claim *	1	
A	FR-A-2 092 822 (BRISTOL-MYERS) * Claim *	1	
			TECHNICAL AREAS SEARCHED (Int. Cl. 4) C 09 K A 61 K

The present report has been established for all claims.

Site of search	Date of completion of search	Examiner
The Hague	05/17/1988	DELANGHE, L.L.M.

CATEGORY OF DOCUMENTS CITED

X:
Y:
A: A technical background
O:
P:

T:
E:
D:
L:
&: